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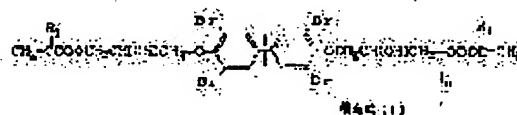
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(54) PHOTO-CURABLE PLASTIC LENS

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a high refractive index photo-curing plastic lens, having low specific gravity and a high Abbe's number, superior in shock resistance, dyeability, transparency, etc., and easy to photopolymerize.

SOLUTION: The photo-curable plastic lens comprises a copolymer obtained by photopolymerizing a composition, consisting of 10-70 wt.% bromine-added bisphenol A-type epoxy (meth)acrylate of formula, 30-90 wt.% another compound having a (meth)acrylic group and 0-50 wt.% monomer copolymerizable with these and has a refractive index of 1.58 or higher, a specific gravity of 1.5 or smaller and an Abbe's number of 30 or larger.



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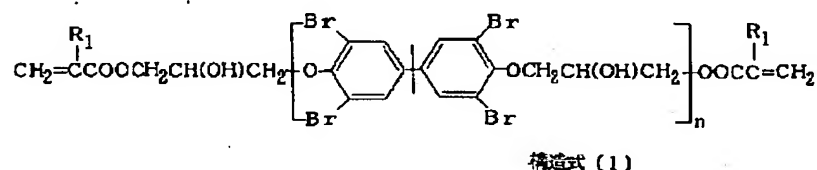
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 CLAIMS

[Claim(s)]

[Claim 1] The lens made of a photo-setting resin which consists of a copolymer obtained by photopolymerizing 30 - 90 % of the weight of compounds which have acrylic (meta) radicals other than this for the bromine addition mold bisphenol A mold epoxy (meta) acrylate expressed with the following structure expression (1) ten to 70% of the weight, and the constituent of 0 - 50 % of the weight of monomers in which these and copolymerization are possible, and is characterized by being 1.58 or more refractive indexes, 1.5 or less specific gravity, and the 30 or more Abbe numbers.

[Formula 1]



(R1 expresses a hydrogen atom or a methyl group among a formula, and n expresses a positive integer.)

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the lens made of synthetic resin, in more detail, since this invention can simplify a production process, it is suitable for mass production method, and relates to the lens made of a photo-setting resin with a high refractive index.

[0002]

[Description of the Prior Art] Before, various inorganic glass and synthetic resin have been used for an optical lens ingredient. Although various physical properties are required of an optical lens ingredient, in the field of a spectacle lens, it is very important that they are a high refractive index, the high Abbe number, and low specific gravity, for example. That is, if the lenses used are a high refractive index and low specific gravity, the thinning of a lens and lightweight-ization will be attained, and if it is the high Abbe number, there is little distribution of light and it is because a comfortable feeling of wearing is obtained.

[0003] In the field of a spectacle lens, there is an ingredient called "CR-39" which uses diethylene-glycol bisallyl carbonate as a raw material as an early typical example as an ingredient of the lens made of synthetic resin. Since it was very lightweight as compared with the inorganic glass lens till then, this ingredient permeated the world quickly. However, this ingredient was not what the whole lens becomes thick since the refractive index is as low as about 1.50, and can never be satisfied as a lens for glasses. Therefore, in order to realize the thinning of a lens, research of a raise in a refractive index was done briskly. In the charge of urethane resin lumber (JP,2-270859,A) obtained by as a result, for example, a thiol, carrying out the polymerization of the isocyanate, 1.60 or more refractive indexes were attained and the thinning of a lens -- 1.70 or more refractive indexes are attained -- was further accelerated quickly at the charge of episulphide resin lumber containing an episulphide compound (JP,9-71580,A). There are actually some which are put in practical use as a high refractive index and super-high refractive-index resin in these.

[0004]

[Problem(s) to be Solved by the Invention] However, an urethane reaction and super-high refractive-index resin are synthetic resin obtained by episulphide ring opening reaction, and above-mentioned high refractive-index resin needed the

synthetic approach by thermal polymerization which both needs long heat-curing time amount. For example, in the field of the lens for glasses, since polymerization time amount was as long as about 20 hours from 10 hours, the time amount which occupies the glass mold used at the time of lens manufacture was also long, and it was not suitable for mass production method.

[0005] On the other hand, the method of manufacturing the lens for glasses using photopolymerization of the time amount which occupies glass mold since polymerization time amount is as short as about several minutes is also short, and it is suitable for mass production method.

[0006] Here, the ingredient (JP,4-57831,A) which prepares a thiol and the precuring product (prepolymer) of a vinyl monomer, for example, and is obtained as an ingredient in which photopolymerization is possible, the ingredient (JP,8-183816,A) using a new sulfur compound, etc. are proposed. Not only thermal polymerization but photopolymerization is a possible high refractive-index ingredient, and these ingredients actually have in these some which have attained 1.60 or more refractive indexes.

[0007] however, with the ingredient prepared and obtained, a thiol and the precuring product of a vinyl monomer, for example In order to require a complicated precuring process on the occasion of photopolymerization, there is a problem that lens production time is seldom shortened, and with the ingredient using a new sulfur compound The present condition is having very many problems -- the new matter, therefore a mass-production-method technique not being established, and the property which specific gravity with high cost is high, and needs it for optical lenses, such as shock resistance, the Abbe number, a dye affinity, and transparency, fully not being acquired moreover. The lens made of a photo-setting resin which adopted photopolymerization is [that the thing of a low refractive index is only put in practical use, and] actually.

[0008] As mentioned above, since there were many troubles -- a problem is in high-volume production capability since the high refractive-index ingredient put in practical use until now is difficult photopolymerization, and production time is seldom shortened in order that the high refractive-index ingredient in which photopolymerization is possible may require the complicated routing which is not fully equipped with the property required for optical lenses, such as shock resistance and the Abbe number -- utilization was very difficult.

[0009] Therefore, the purposes of this invention are low specific gravity and the high Abbe number, and are to excel in shock resistance, a dye affinity, transparency, etc., and offer the lens made of a high refractive-index photo-setting resin with easy photopolymerization.

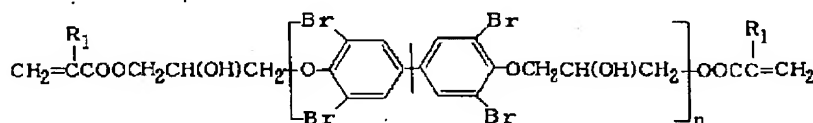
[0010]

[Means for Solving the Problem] the resin obtained by photopolymerizing the ingredient which used the acrylic (meta) compound of specific structure as the indispensable component as a result of this invention persons' repeating examination wholeheartedly to such the present condition -- a high refractive index -- attaining -- in addition -- and the thing which were fully equipped also with the property required for an optical lens and which is excelled very much is found out, and it comes to complete this invention.

[0011] That is, this invention is a lens made of a photo-setting resin which consists of a copolymer obtained by photopolymerizing 30 – 90 % of the weight of compounds which have acrylic (meta) radicals other than this for the bromine addition mold bisphenol A mold epoxy (meta) acrylate expressed with the following structure expression (1) ten to 70% of the weight, and the constituent of 0 – 50 % of the weight of monomers in which these and copolymerization are possible, and is characterized by being 1.58 or more refractive indexes, 1.5 or less specific gravity and 30 or more Abbe numbers.

[0012]

[Formula 2]



構造式 (1)

(R1 expresses a hydrogen atom or a methyl group among a formula, and n expresses a positive integer.)

In this invention, the resin which has the physical properties which were excellent the account of a top can be easily mass-produced in a short time by photopolymerizing the constituent with which photopolymerization consists of an easy specific constituent.

[0013]

[Embodiment of the Invention] The photo-setting resin of this invention contains preferably the bromine addition mold bisphenol A mold epoxy (meta) acrylate of a structure expression (1) 20 to 60% of the weight ten to 70% of the weight. This reason is that it becomes difficult to attain the high refractive index which is the description of this invention when bromine addition mold bisphenol A mold epoxy (meta) acrylate is less than 10 % of the weight, and is because the viscosity of this component is very high when exceeding 70 % of the weight, so handling becomes very difficult.

[0014] Moreover, the photo-setting resin of this invention contains preferably the compound which has acrylic (meta) radicals other than the above 40 to 80% of the weight 30 to 90% of the weight. This reason is because handling not only becomes difficult, but it becomes difficult to acquire a property required for optical lenses, such as thermal resistance and shock resistance, since viscosity becomes high at less than 30% of the weight of a case, and when exceeding 90 % of the weight, it is because it becomes difficult to attain the high refractive index which is the description of this invention. The number of them does not necessarily need to be one, and since the compound which has an acrylic (meta) radical at this time gives various properties to the resin obtained, it can also combine two kinds or more than it.

[0015] Although anythings do not interfere, the compound containing the acrylic (meta) radical at this time has the very desirable thing of a high refractive index and hypoviscosity, in order to attain the high refractive index which is the description of this invention, and the simple nature of handling. As an example,

hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA), Monofunctional acrylic compounds, such as 2-phenylphenol poly ethoxy acrylate (OPP), Neopentyl glycol diacrylate (NPG), polyethylene-glycol diacrylate (PEDA), Tetramethylolmethane triacrylate (TMM), a bis--2-acryloyl thio ethyl sulfide (A-TES), Polyfunctional acrylic compounds, such as 1 and 4-bis-acryloyl thio benzene (BATB), Hydroxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA), Monofunctional methacrylic compounds, such as benzyl methacrylate (BZMA), 2-hydroxy - 1, 3-dimethacrylate (HDP), 2,2-bis(4-methacryloxypolyethoxyphenyl) propane (BPE), Although polyfunctional methacrylic compounds, such as trimethylolpropanetrimethacrylate (TMPT), bis--2-methacryloyl thio ethyl sulfide (TES), 1, and 4-bis-methacryloyl thio benzene (BMTB), are mentioned, it is not limited to these.

[0016] Moreover, the photo-setting resin of this invention can add the monomer in which those components and copolymerization other than the above-mentioned component are possible as occasion demands, in order to give various properties to the resin obtained. However, since obtaining as an optical lens becomes difficult when it adds exceeding 50 % of the weight, an addition is 0 - 50 % of the weight. The number of the monomers at this time does not necessarily need to be one, and they can also combine two kinds or more than it.

[0017] The monomer at this time has the desirable thing of a high refractive index and hypoviscosity, in order to attain the high refractive index which is the description of this invention, and the simple nature of handling although anythings do not interfere if the above-mentioned component and copolymerization are possible. As an example, although polyfunctional thiols, such as allyl ester, such as vinyl compounds, such as styrene (St) and an alpha-methyl-styrene dimer (MSD), allyl benzoate (AKA), and diallyl phthalate (FDA), pentaerythritol tetrakis thio GURIKONETO (PETG), and pentaerythritol tetrakis thiopropionate (PETP), and others are mentioned, it is not limited to these.

[0018] The photo-setting resin of this invention can be manufactured [which can perform a polymerization collectively since the fluidity is able to make viscosity of a constituent low and to change into sufficient condition with the combination of each above-mentioned component, for example, after pouring into a casting container / therefore / easy and] by low cost.

[0019] It has the description for this invention to be a copolymer obtained by photopolymerizing the constituent which consists of the above.

Photopolymerization can apply a well-known photopolymerization technique. That is, after pouring a constituent into a casting container etc., for example, the copolymer by which macromolecule quantification was carried out can be obtained by the approach of irradiating beams of light, such as ultraviolet rays and an electron ray.

[0020] It is possible to add a photopolymerization initiator (photosensitizer) as occasion demands in photopolymerization at this time. For example, in order to obtain a copolymer more in the case where photopolymerization is performed by the approach of irradiating ultraviolet rays for a short time, it is desirable to add a photopolymerization initiator in a constituent beforehand. The number of the photopolymerization initiators added at this time does not necessarily need to be

one, and they can be used combining two kinds or more than it as occasion demands. However, since a property required for optical lenses, such as a refractive index and shock resistance, falls when there are too many additions, the addition of a photopolymerization initiator has 10 or less desirable % of the weight, and it is 8 or less % of the weight more preferably.

[0021] As a photopolymerization initiator at this time, well-known photopolymerization initiators, such as acetophenones and benzophenones, are usable. As an example of a photopolymerization initiator, although alpha-hydroxy isobutyl phenon, a benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, a 2-hydroxy-2-benzoyl propane, benzyl dimethyl ketal, thioxan, 2-chloro thioxan ton, azobisisobutyronitril, etc. are mentioned, it is not limited to these.

[0022] Moreover, it is possible to make the constituent at this time contain a coloring agent, a thermostabilizer, and other auxiliary materials beforehand if needed. Furthermore, it is also possible to give the surface coat of a rebound ace court agent, a nonreflective coat, and others to the front face of the obtained copolymer.

[0023] The photo-setting resin of this invention can be manufactured also by the approach of beginning to delete, after having the description for it to be the copolymer obtained as mentioned above, therefore obtaining the copolymer of a plate and others besides a casting polymerization method.

[0024]

[Example] Hereafter, although an example explains in more detail, this invention is not limited to these. In addition, the evaluation approach of many acquired physical properties is as follows.

[0025] The refractive-index 10mmx20mmx3mm test piece was created, alpha-promo naphthalene was used for contact liquid using the product "DR-M2" made from ATAGO, and the refractive index in a room temperature (20 degrees C) was measured.

[0026] The Abbe number was measured with the same measuring device as the refractometry of the Abbe number above, and the measuring method.

[0027] The specific gravity 10mmx20mmx3mm test piece was created, and specific gravity was measured using the product "SGM-6" made from METORATORED.

[0028] Ten samples for a trial of the shock-proof diameter of 78mm, the radius of curvature of 0.1m, and 2mm of main thickness were produced, the shot with a weight of 16.2g (diameter of about 1.59cm (10/16 inch)) was dropped from height of 1.27m to this, what did not break ten sheets was made good according to the specification of the FDA drop impact strength, and the thing broken at least one sheet was made into the defect.

[0029] The stain solution was created by mixing 1g of SEIKO plaque SUBURAUN and the assistants by SEIKO CORP. to 1000ml of dye affinity pure water, respectively, it dyed by dipping the obtained lens in the stain solution for 10 minutes at 92 degrees C, and total light transmission was measured using ultraviolet [by Shimadzu Corp.], and a visible spectrophotometer "UV-2200", 40% or less of thing was made good, and the thing exceeding 40% was made into the defect.

[0030] The plate of 2.0mm of transparency core thickness was created, the haze was measured using "HGM-2DP" by Suga Test Instruments Co., Ltd., the 0.3 or less-haze thing was made good, and the thing exceeding 0.3 was made into the defect.

[0031] (Example 1) Bromine addition bisphenol A mold epoxy acrylate (BRA) 30g and TES are measured to 40g, the above was measured for 30g and BPE to 200ml beaker, after adding IRGACURE184 [1000 ppm] (Ciba-Geigy Japan make) of a photopolymerization initiator and fully agitating it, it poured into the casting mold which consisted of a glass plate of two sheets, and a gasket, and the black light performed the ultraviolet-rays polymerization on condition that quantity-of-radiation 800 mW/cm², the irradiation range of 50cm, and irradiation time 10min. The copolymer was picked out from casting mold after that, and the finished product was obtained.

[0032] The obtained copolymer is a physical-properties value like a Table 1 publication, and mold goods with good 1.58 or more refractive indexes, 30 or more Abbe numbers, 1.50 or less specific gravity and shock resistance, dye affinity, and transparency were obtained.

[0033] (Examples 2-5) The polymerization constituent was mixed by the presentation ratio shown in Table 1, after adding IRGACURE184 [1000 ppm] (Ciba-Geigy Japan make) of a photopolymerization initiator and fully agitating it, it poured into the casting mold which consisted of a glass plate of two sheets, and a gasket, and the black light performed the ultraviolet-rays polymerization on condition that quantity-of-radiation 800 mW/cm², the irradiation range of 50cm, and irradiation time 10min. The copolymer was picked out from casting mold after that, and the finished product was obtained.

[0034] The obtained copolymer was able to acquire the physical-properties value as shown in Table 1, respectively. In the examples 2-5, each is 1.58 or more refractive indexes, the 30 or more Abbe numbers, and 1.50 or less specific gravity, and mold goods with good shock resistance, dye affinity, and transparency were obtained.

[0035] (Example 1 of a comparison) As shown in the example 1 of a comparison of Table 1, bromine addition bisphenol A mold epoxy acrylate performed the same photopolymerization as the above-mentioned example by the presentation exceeding 70 % of the weight. consequently, specific gravity -- 1.50 -- exceeding -- in addition -- and the total light transmission after dyeing is 40% or more, and the problem was checked by specific gravity and the dye affinity. Moreover, also about handling, since viscosity was very high, handling was difficult.

[0036] (Example 2 of a comparison) As shown in the example 2 of a comparison of Table 1, the same photopolymerization as the above-mentioned example was performed for bromine addition bisphenol A mold epoxy acrylate by less than 10% of the weight of the presentation. Consequently, a refractive index is less than 1.58 and the problem was checked by the refractive index.

[0037] (Example 3 of a comparison) As shown in the example 3 of a comparison of Table 1, the same photopolymerization as the above-mentioned example was performed by the presentation whose acrylic (meta) compound exceeds 90 % of the weight. Consequently, in order that an methacrylic compound might exceed 90 % of

the weight, the content of bromine addition bisphenol A mold epoxy acrylate decreased relatively, the refractive index became less than 1.58 as the result, and the problem was checked by the refractive index.

[0038] (Example 4 of a comparison) As shown in the example 4 of a comparison of Table 1, the acrylic (meta) compound performed the same photopolymerization as the above-mentioned example by less than 30% of the weight of the presentation. Consequently, the room temperature of a degree of hardness is also so inadequate that it is soft, and each physical properties were not able to be measured, either.

[0039] (Example 5 of a comparison) As shown in the example 5 of a comparison of Table 1, the same photopolymerization as the above-mentioned example was performed by presentation whose monomers other than an acrylic (meta) compound exceed 50 % of the weight. Consequently, the room temperature of a degree of hardness is also so inadequate that it is soft, and each physical properties were not able to be measured, either.

[0040]

[Table 1]

表1

		実 施 例					比 較 例				
		1	2	3	4	5	1	2	3	4	5
組 成	BRA	30	40	40	30	40	80	8	8	40	10
	BPE	30	—	10	—	10	10	40	46	20	30
	TES	40	30	—	30	—	—	—	—	—	—
	BzMA	—	30	40	30	30	10	40	46	—	—
	St	—	—	—	—	10	—	—	—	20	30
	PETP	—	—	10	10	10	—	12	—	20	30
物 性	屈 折 率	1.584	1.599	1.581	1.596	1.582	1.590	1.561	1.558	レンズ 化不能	レンズ 化不能
	アッペ数	38.8	37.2	34.2	37.8	33.2	31.8	38.8	37.2		
	比 重	1.382	1.392	1.386	1.374	1.368	1.520	1.284	1.268		
	耐衝撃性	良好	良好	良好	良好	良好	良好	良好	良好		
	染色性	良好	良好	良好	良好	良好	不良	良好	良好		
	透明性	良好	良好	良好	良好	良好	良好	良好	良好		

BRA : 臭素付加型ビスフェノールAエポキシアクリレート
 BPE : ビスメタクリロキシポリエトキシフェニルプロパン
 TES : ビスメタクリロイルチオエチルスルフィド
 BzMA : ベンジルメタクリレート
 St : スチレン
 PETP : ペンタエリスリトールテトラキスチオプロピオネート

[0041]

[Effect of the Invention] This invention can manufacture the optical lens of a high refractive index easily in a short time by copolymerizing the ingredient with which photopolymerization consists of an easy specific constituent. Namely, each physical properties, such as transparency, a dye affinity, and shock resistance, are not only good, but can mass-produce a lens with a high refractive index easily at a short time and the simplified process.

[Translation done.]